

XXVI.—*The Colouring Matters of the Indian Dye Stuff*
Asbarg, Delphinium zalil.

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ASBARG consists of the dried flowers and flowering stems of *Delphinium zalil*, a perennial, herbaceous plant belonging to the *Ranunculaceæ*, which is found in great quantity in Afghanistan. Dr. Aitchison says of it (Watts' *Dictionary of the Economic Products of India*, 1890, 3, p. 70): "This plant forms a great portion of the rolling downs of the Badghis; in the vicinity of Gulran it was in great abundance and when in blossom gave a wondrous golden hue to the pastures; in many localities in Khorassan of about 2000 feet altitude, it is equally common."

The dried fragments and flowering stems are taken to Multan and other Punjab towns, from which they are conveyed all over India. It is much used in silk dyeing for the production of a sulphur-yellow colour known as "gandhaki," and together with *Datisca cannabina* to

obtain a similar shade on alum mordanted silk; it is also used in calico printing. The flowers, which are bitter, are likewise employed medicinally as a febrifuge.

No examination of the colouring matter of this dye stuff appears to have been previously made, although an account of its tinctorial properties has been communicated to the Society of Chemical Industry (*J. Soc. Ch. Ind.*, 1895, 14, 458) by J. J. Hummel and one of us. Our thanks are due to the authorities of the Imperial Institute, who, on the application of Professor Hummel, were good enough to procure a considerable quantity of this material for our investigation.

EXPERIMENTAL PART.

At the commencement of this investigation, the flowers and flowering stems of the plant were examined together, but the latter, being practically devoid of dyeing property, were subsequently discarded, an economy of labour being thus effected. Various methods suggested themselves for the isolation of the colouring matter, which exists here entirely as a glucoside, and ultimately the following was adopted.

The dye stuff was extracted with ten times its weight of boiling water, the mixture strained through calico, and the filtrate, after treatment with a little sulphuric acid, was again boiled for 15 minutes. The decomposition of the glucosides is very readily effected, and the action should not be prolonged, otherwise a tarry product is formed, which is a great hindrance in the later processes. On cooling, a brownish-yellow powder separated, which was collected, drained upon a porous tile, and when dry digested with boiling alcohol which dissolved the colouring matter, leaving a considerable residue of calcium sulphate. The dark coloured solution, after being evaporated to a small bulk, was poured into a large volume of ether, the mixture washed with water until the washings were colourless, and then agitated with dilute alkali to free the substance from a wax which alone remained in the ether after this treatment. On acidifying the alkaline liquid, it deposited yellow flocks of the colouring matter still contaminated with some impurity of an acid nature; to remove this, excess of sodium hydrogen carbonate was added to the mixture, and the product extracted with ether; this now dissolved nothing but the colouring matter, and the latter, on evaporation, was left of a pure yellow colour.

Sparingly soluble Colouring Matter.

It was evident on examination that the product thus obtained contained two colouring matters at least, one of which was distinguished by its sparing solubility in alcohol. After being isolated by this means it was converted into its acetyl derivative, which was recrystal-

lised, and then decomposed in the usual manner, the regenerated colouring matter being finally crystallised from acetic acid.

0.1164 gave 0.2598 CO_2 and 0.0400 H_2O . C = 60.86 ; H = 3.81.

$\text{C}_{16}\text{H}_{12}\text{O}_7$ requires C = 60.76 ; H = 3.79 per cent.

It formed a glistening mass of yellow needles, resembling rhamnetin in appearance, very sparingly soluble in boiling alcohol or acetic acid. With lead acetate in alcoholic solution, an orange-red precipitate was formed, whilst ferric chloride gave a greenish-black coloration. With the haloid acids, in the presence of acetic acid, no compounds of the acids were produced ; sulphuric acid also reacted with difficulty, and owing to the small yield and the instability of the product thus obtained, it was not further examined.

Fusion with Alkali.—The colouring matter was digested with very concentrated potassium hydroxide solution at 200—220° for 1 hour, and the brown melt dissolved in water ; the green solution was then neutralised with acid, extracted with ether, and the extract evaporated. The residue, after being dissolved in water, was treated with lead acetate, and the yellowish-white precipitate thus produced was collected, washed, and decomposed with dilute sulphuric acid. From the clear liquid, ether extracted a crystalline acid, soluble in dilute alkali to form a green liquid which became brown on exposure to air. The acid was now dissolved in water, and the solution saturated with salt, causing the separation of a trace of a viscous product which was removed by filtration. The filtrate was extracted with ether, and the residue obtained on evaporation purified by crystallisation from water. With dilute alkali, this product now yielded a colourless solution, and examination showed that the green coloration previously obtained in this manner was due to the impurity removed by the salt treatment.

0.1135 gave 0.2275 CO_2 and 0.0400 H_2O . C = 54.66 ; H = 3.91.

$\text{C}_7\text{H}_6\text{O}_4$ requires C = 54.54 ; H = 3.90 per cent.

It crystallised in colourless needles melting at 194—196°, gave a green coloration with aqueous ferric chloride, and evidently consisted of *protocatechuic acid*.

The filtrate from the lead precipitate was treated with sulphuric acid, filtered from lead sulphate, neutralised with sodium hydrogen carbonate, and extracted with ether. The crystalline residue left on evaporation, when purified, melted at 210°, and was found to be *phloroglucinol*.

The substance which gave the green coloration when the melt was dissolved in water could not be isolated in a pure condition, the quantity present being very small. In a second experiment, employing a new preparation of the colouring matter, this substance was

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not detected, and it was thought that the green coloration had been due to an impurity. It appeared subsequently, however, that the condition necessary for its production was the use at the first of a comparatively dilute caustic alkali solution, preferably four parts of alkali in one of water. It is evident, therefore, that the reaction is characteristic of this colouring matter.

Action of Hydriodic Acid.—The similarity of this substance to rhamnetin, especially in its behaviour towards mineral acids, suggested that it contained a methoxy-group. Examination by Zeisel's method proved this to be the case.

0.1750 gave 0.1310 AgI. $\text{CH}_3 = 4.77$.

$\text{C}_{15}\text{H}_9\text{O}_6(\text{OCH}_3)$ requires $\text{CH}_3 = 4.74$ per cent.

To the hydriodic acid residue, after dilution with water, sodium hydrogen sulphite solution was added, and the yellow, flocculent product collected and crystallised from dilute alcohol.

0.1021 gave 0.2242 CO_2 and 0.0345 H_2O . $\text{C} = 59.88$; $\text{H} = 3.75$.

$\text{C}_{15}\text{H}_{10}\text{O}_7$ requires $\text{C} = 59.60$; $\text{H} = 3.31$ per cent.

The product from a second experiment was acetylated, and the colourless substance, which melted at $189-191^\circ$, was analysed.

0.1165 gave 0.2494 CO_2 and 0.0462 H_2O . $\text{C} = 58.38$; $\text{H} = 4.40$.

$\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$ requires $\text{C} = 58.59$; $\text{H} = 3.90$ per cent.

The above results, and the fact that the methyl ether when fused with alkali gives phloroglucinol and protocatechuic acid, indicated that this substance, $\text{C}_{15}\text{H}_{10}\text{O}_7$, was *quercetin*. An examination of its general properties corroborated this view. It is thus evident that the sparingly soluble colouring matter of *Delphinium zaili* is a *quercetin monomethyl ether*.

Acetyl Compound.—To confirm the above results, and to determine if this colouring matter was identical with either of the two known methyl ethers of quercetin (rhamnetin and iso-rhamnetin), it was acetylated in the usual manner, and the product crystallised from alcohol.

0.1213 gave 0.2650 CO_2 and 0.0445 H_2O . $\text{C} = 59.57$; $\text{H} = 4.07$.

$\text{C}_{16}\text{H}_8\text{O}_7(\text{C}_2\text{H}_3\text{O})_4$ requires $\text{C} = 59.50$; $\text{H} = 4.13$ per cent.

A determination of the methoxy-group gave the following result.

0.2076 gave 0.0880 AgI. $\text{CH}_3 = 2.70$.

Theory requires $\text{CH}_3 = 3.09$ per cent.

Liebermann's method was employed for the estimation of the acetyl groups.

1.0740 gave 0.7047 $C_{16}H_{12}O_7$. Found 65.61.

The theory for four acetyl groups requires $C_{16}H_{12}O_7 = 65.29$ per cent.

It formed a glistening mass of colourless, hair-like needles, melting at 195—196°, identical in appearance and general properties with acetyliso-rhamnetin. The sparingly soluble colouring matter of the *Delphinium zalil* is, therefore, *iso-rhamnetin*, a substance but recently isolated for the first time (Trans., 1896, 69, 1650) from the petals of the yellow wallflower (*Cheiranthus Cheiri*). The difficulty of obtaining a sufficient supply of raw material did not allow at that time of the determination of the position of the methoxyl group in this colouring matter. Experiments were, therefore, now instituted with this object.

Methylation of Iso-rhamnetin.—As in the case of rhamnazin (quercetin dimethyl ether) (Trans., 1897, 818), this reaction was studied, for should the methoxy-group be present in the ortho-position relatively to the carbonyl group, a quercetin pentamethyl ether might be produced, and not the tetramethyl compound, which is always formed when quercetin itself is so treated.

Iso-rhamnetin (1 mol.) dissolved in a solution of potassium hydroxide (4 mols.) in methylic alcohol was digested with excess of methylic iodide for 24 hours. After removal of the unattacked iodide and excess of alcohol, the residue was dissolved in ether, and the solution washed with dilute alkali and evaporated; the product, after crystallisation from acetone, formed pale yellow needles melting at 154—156°.

0.1170 gave 0.2745 CO_2 and 0.0543 H_2O . $C = 63.98$; $H = 5.15$.

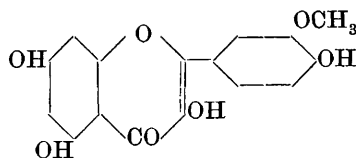
$C_{15}H_6O_3(OCH_3)_4$ requires $C = 63.69$; $H = 5.03$ per cent.

It was found to consist of *quercetin tetramethyl ether*.

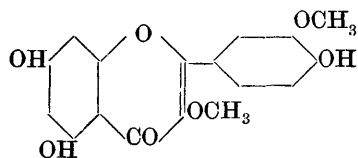
Oxidation of Iso-rhamnetin.—The previous experiment having given a negative result, it was necessary to determine if the methoxyl group was present in the catechol nucleus. For this purpose, air was aspirated through a dilute alkaline solution of the colouring matter until this, which was at first yellow, had become brown, and on treatment with acids no longer yielded a precipitate; the liquid was then neutralised with acid, treated with excess of sodium hydrogen carbonate, extracted with ether (A), and again acidified and extracted with ether (B). The latter extract, on evaporation, deposited crystals which were purified by recrystallisation from water until colourless; a lustrous mass of needles was thus obtained, which dissolved sparingly in cold water, gave no reaction with ferric chloride, and melted at 206—207°. This substance was *vanillic acid*, and the locality of the methoxy-group in iso-rhamnetin is thus evident. On evaporating extract (A), a residue was left having the reactions of *phloroglucinol*.

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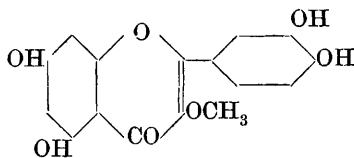
Employing the constitution assigned to quercetin by Herzig, that of iso-rhamnetin may be expressed as follows.



Consequently rhamnazin (*loc. cit.*), a quercetin dimethyl ether, is closely related to iso-rhamnetin and to rhamnetin, it being a mono-methyl ether of both these colouring matters.



Rhamnazin.



Rhamnetin.

Dyeing Properties.—A comparison was made of the tinctorial properties of iso-rhamnetin and quercetin, woollen cloth mordanted with aluminium, tin, chromium, and iron being employed for this purpose. The shades obtained were as follows.

	Aluminium.	Tin.	Chromium.	Iron.
Iso-rhamnetin	Lemon yellow.	Orange yellow.	Orange brown.	Pale brown olive.
Quercetin ...	Brown orange, inclining to yellow.	Bright orange.	Red brown.	Green black.

These results are interesting, as they indicate the effect of neutralising the two ortho-hydroxyls of quercetin by the conversion of one of them into a methoxy-group. As previously discussed (*Trans.*, 1897, 71, 818), the presence of these hydroxyls in quercetin enhances its tinctorial value, although iso-rhamnetin is again an instance that such a property is not essential to the dyes of this group. The shades produced are weaker than those given by quercetin, but considerably stronger than those given by rhamnazin, which is a very feeble dye; they somewhat closely resemble, especially in the yellow tint with aluminium mordant, that yielded by chrysin and apigenin in a similar way. Unlike these latter, however, it is capable of dyeing with a tin mordant. It is interesting to note that little evidence is now required for a complete study of the shade effect caused by the various hydroxyls existing in quercetin.

Readily soluble Colouring Matter.

The alcoholic mother liquors obtained during the isolation and purification of the above colouring matter were evaporated to half their bulk, and the small quantity of impure iso-rhamnetin which separated on long standing removed by filtration, and the filtrate treated with boiling water. On cooling, a yellow, crystalline product was deposited, which was collected and a portion acetylated, in the hope that this would lead to its identification. The colourless needles thus obtained had, however, no definite melting point, indicating a mixture, for they softened below 100° , and did not fuse completely until about 160° . It has been recently shown in a communication to the Society (Proc., 1898, 56), that various yellow colouring matters in alcoholic solution decompose potassium acetate with the production of insoluble salts, although this behaviour is not common to all of them. Fractional crystallisation having failed to effect a separation of these colouring matters, recourse was had to this reaction, in the hope that one only would form an insoluble product. A hot concentrated alcoholic solution of the substance was, therefore, boiled with a small quantity of potassium acetate for a few minutes, and the crystals which gradually separated were collected, washed with alcohol, and decomposed with acid. The regenerated colouring matter was further purified by suspending it in acetic acid and adding sulphuric acid, and the deposited acid compound was then collected, washed with acetic acid, and decomposed in the usual manner.

0.1200 gave 0.2620 CO_2 and 0.0410 H_2O . $\text{C} = 59.54$; $\text{H} = 3.79$.

$\text{C}_{15}\text{H}_{10}\text{O}_7$ requires $\text{C} = 59.60$; $\text{H} = 3.31$ per cent.

It formed glistening needles, an alcoholic solution of which gave an orange-red precipitate with lead acetate, and with ferric chloride a dark green coloration. The *acetyl compound* was obtained as colourless needles melting at $189-191^{\circ}$.

0.1182 gave 0.2518 CO_2 and 0.0425 H_2O . $\text{C} = 58.09$; $\text{H} = 3.99$.

$\text{C}_{15}\text{H}_5\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$ requires $\text{C} = 58.59$; $\text{H} = 3.90$ per cent.

As fusion with alkali yielded *protocatechuic acid* and *phloroglucinol*, this colouring was evidently *quercetin*.

To obtain, if possible, some clue as to the nature of the substance previously associated with the quercetin and which did not react with potassium acetate, the filtrate from the potassium quercetin was first saturated with the acetate, any deposited salt thus produced being removed by filtration; the filtrate was then acidified, treated with boiling water, and the crystals which separated collected, washed, and dried. Experiments with this product gave results which indicated that

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it was not homogeneous, but as the quantity available was very small no further attempts at purification could be carried out with advantage. On analysis, it yielded numbers C = 59·8, H = 3·90, somewhat similar to those required for quercetin, C = 59·60, H = 3·31. Its acetyl derivative, which formed colourless needles, behaved peculiarly when heated, for it fused entirely at 118—120°, then gradually solidified, and melted again at 179—180°. A portion which had melted at the lower temperature and again solidified, after recrystallisation, behaved in an identical manner. Analysis gave C = 58·54, H = 4·24. Acetyl-quercetin requires C = 58·59, H = 3·90 per cent. On fusion with alkali, it yielded *phloroglucinol* and *protocatechuic acid*.

These results indicate a close similarity between this colouring matter and quercetin, and it would appear that it was merely the latter in an impure condition. Should this be the case, it is difficult to understand that so small an amount of impurity could account for its not giving an insoluble potassium salt when treated with potassium acetate, and also for the melting point of its acetyl derivative. Further study of this substance must be discontinued for the present, owing to the exhaustion of our supply of material.

The Dyeing Properties of Asbarg.

In the previous communication on this subject (*loc. cit.*), it was shown that a close resemblance exists in this respect between asbarg and quercitron bark, although the former yields, with aluminium mordant, a purer or less orange yellow. It is, however, a much weaker dye stuff, having but 35 per cent. the dyeing power of quercitron bark. As the above experiments were carried out with the material in the condition received from the Imperial Institute, further trials were instituted with a sample from which the worthless flowering stalks had been removed. The shades obtained with this product on wool mordanted in the usual manner are given below; they still indicated a lack of dyeing power as compared with quercitron bark.

	Aluminium.	Chromium.	Iron.	Tin.
Asbarg	Golden yellow.	Brownish orange.	Brown olive.	Bright orange.
Quercitron bark	Brown yellow.	Deep brown orange.	Olive black.	„

Percentage of Colouring Matter.—An examination of asbarg, minus the flowering stalks, showed that it contained 3·47 per cent. of colouring matter (not as glucoside). The estimation was carried out by a method we have lately devised for this purpose, and which we are

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applying to the estimation of colouring matter in dye stuffs of the quercitron class. The details of the method are not given here, for we hope to make a communication on this subject at a later date.

An examination of the blue flowers of *Delphinium consolida* has shown that these contain, curiously enough, some quantity of yellow colouring matter; this, however, is not identical with that present in *Delphinium zaili*. The study of this product, which is at present delayed owing to lack of raw material, will be shortly continued.

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